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INVES'I'IGATION OF THE ANTIMONY-RICH PART OF THE Ru-Sb SYSTEM

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1. Introduction

The Ru-Sb phase diagram is not available and very little information is known about this system, Two compounds between antimony and ruthenium have been previously reported: $RuSb_2$ with the FeS_2-*m* (*m* =marcasite) structure [1,2] and RuSb with the MnP structure [3,4]. $RuSb_2$ is orthorhombic with a = 5.9524 Å, b = 6.6737 Å and c = 3.1803 Å [2] and, according to X-ray measurements, the homogeneity range of this compound is from 66 to 67.5 at.% Sb [2]. RuSb is orthorhombic with a = 5.9608 Å, b = 3.7023 Å and c = 6.5797 Å [4].

This study resulted from our interest in the compound $RuSb_2$ as potential semiconductor and thermoelectric material. The electrical properties of $RuSb_2$ have not been investigated so far, In order to grow crystals of this compound from the melt, the knowledge of the phase diagram is necessary. Therefore, we determined part of the Ru-Sb system on the antimony-rich side.

2. Experimental

Alloys in the composition range 60 to 95 at.% Sb were prepared for Differential Thermal Analysis (DTA) and also optical and microprobe investigations. The alloys were synthesized in scaled quartz ampoules from stoichiometric amounts of high purity antimony (99.9999%) and ruthenium (99.997%). The ampoules were heated in a resistance furnace, held at 1250°C for one day.

A Dupont 1600°C DTA furnace was used for the DTA measurements. The samples were sealed under 10-5 Torr vacuum in quartz capsules of 5 mm in diameter and 15 mm long. The rounded bottom of the capsule was flattened and thinned by grinding and fire polishing to provide a better thermal contact between the material and the thermocouple. Argon was used as the purge gas and heating and cooling rates were both 2°C/minute. Analysis of the heating curves determined the temperature values of the solid-liquid transformations within ± 5°C.

Samples of $RuSb_2$ were also prepared afterward by the gradient freeze technique using a two zone Bridgman-like furnace built with a SiC heater as upper heater and a conventional wire heater for the lower zone. The growth of $RuSb_2$ was done in sealed quartz ampoules (12 mm in diameter) which remained stationary during the growth process. ingots of $RuSb_2$ weighing about 4 gms were grown from antimony-rich solutions with an axial temperature gradient of 40 °C/cm and a growth rate of 1 mm/day. Resulting ingots were typically composed of two parts: a lower part corresponding to a single phase material and an upper part which was a mixture of two phases.

Microstructure of the samples, polished by standard metallographic techniques, were investigated using an optical Nikon microscope under both ordinary and polarized light. Microprobe analysis (MPA) of selected samples was also performed on JEOL JXA -733 superprobe. X-ray diffraction (XRD) analysis was conducted on some samples grown by the gradient freeze technique using a Siemens D-500 diffractometer with the Cu-K_α radiation. Powder X-ray patterns were taken with steps scan interval of 2θ = 0.05 and counting time of 3 seconds. The density of several samples were measured by the immersion technique using toluene as the displacement liquid.

3. Results and discussion

The results of the investigation are summarized in Figure 1. Square symbols represent the results obtained by MPA while circles represent the results of DTA measurements. The determination of the liquidus curve above 1250°C was not possible because of the use of quartz vessels for the DTA experiments. 'l'he DTA curves of alloys in the range 70 to 95 at. % Sb registered eutectic transformations at a temperatureof617°C, Figure 2 shows the microstructure of a sample with 80 at. % Sb after DTA measurement, Shaped crystals can be seen within the antimony matrix and all the alloys containing more than 70 at.% Sb showed the same microstructure. The number of precipitated crystals increased with increasing ruthenium concentration. MPA anal ysis showed that the composition of these crystals for the alloy with 80 at. % Sb (Fig. 2) corresponded to a concentration of 68 at.% Sb.

Several $RuSb_2$ samples were grown from two different antimony-rich Ru solutions: 95 and 90 at. % Sb. The corresponding liquidus temperatures of the nominal alloy compositions used, obtained by DTA, were found to be 1000 and 1075°C, respective] y. The lower parts of the grown ingots were single crystalline and one of the ingots tip was ground and analyzed by XRD. The X-ray spectrum generated from the powder corresponded to the marcasite structure of $RuSb_2$. MPA analysis of the ingots tips revealed that their composition corresponded to a concentration of 68.1 and 68 at.% Sb, respectively. These stoichiometric deviations are in agreement with the results of Holseth et al[2] who found a maximum deviation of 67.5 at. % on the antimony-rich side. An average experimental density of 8.893 g/cm^3 (98.1 % of the theoretical density for the 1:2 composition: 9.062 g/cm^3) was measured on several samples grown from the antimony-rich solution with 95 at, % Sb. The average density of the samples grown from the solution with 92.5 at% Sb was found to be 8.92 g/cm^3 (98.4 % of the theoretical density).

Because single crystals of $RuSb_2$ were obtained from a solution corresponding to a liquidus temperature of 1075°C, the melting (decomposition) of this compound should be higher than 1075°C. The DTA curve of a single phase sample of $RuSb_2$ grown by the gradient freeze technique did not show any transformation up to 1250°C. It is also more likely that the melting (decomposition) point of RuSb should be higher than 1250°C. The stoichiometric deviations of RuSb have not been studied.

4. **Conclusion**

The present investigation allowed the determination of the Ru-Sb phase diagram cm the Sb-rich side. The existence oft wo compounds previously reported has been confirmed: RuSb and $RuSb_2$. The phase diagram is composed of a degenerate eutectic on the Sb-rich side at a temperature of 617°C. Stoichiometric deviations up to 68 at.% Sb have been found for $RuSb_2$ and this compound was found to be stable at least to 1250°C.

REFERENCES

1, Kuz'min, R. N., N. N. Zhuravlev, and S. A. Losievskaya, *Soviet Phys. Cryst.*, 5, 202-206 (1960).

2. Holseth H., Kjekshus, A., *Acts Chemica Scandinava ,22,3273-3283* (1968).

3. Zhuravlev N. N., G. S. Zhdanov, and R. N. Kuz'min, *Soviet Phys. Cryst.*, 5, 532-539 (1961).

4. Endresen K., *Acta Chemica Scandinavia, 31,249-252 (1977).*

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FIGURES CAPTIONS

Figure 1: Part of the Ru-Sb phase diagram on the antimony-rich side.

Figure 2: Microstructure of an alloy with 80 at.% Sb after DTA (X 380).

Figure 1

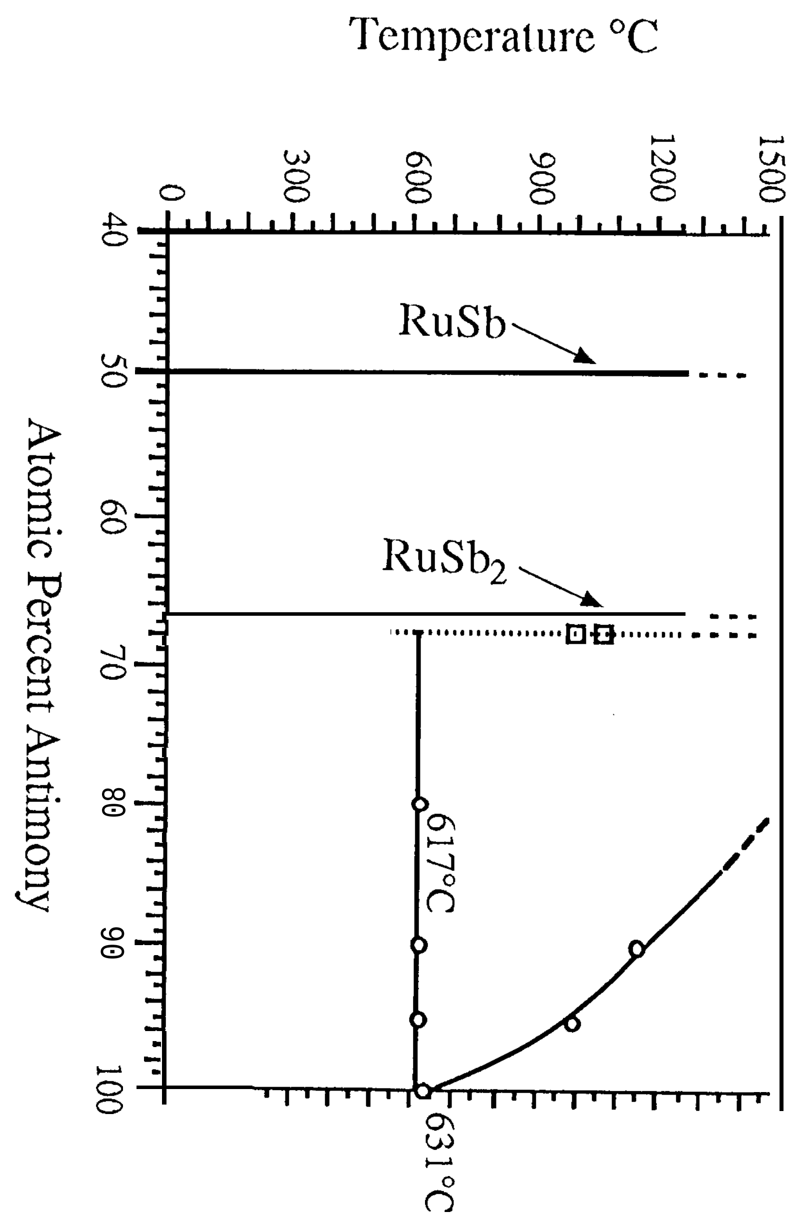
Temperature °C
0
300
600
900
1200
1500
RuSb
$RuSb_2$
617°C
631°C
40
50
60
70
80
90
100
Atomic Percent Antimony

Figure 2